

Advanced Low-Temperature Sorbents for Fluid-Bed Applications

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Abstract

The Integrated Gasification Combined Cycle (IGCC) process is emerging as the most promising technology for advanced electric power generation from coal that is likely to replace conventional coal combustion. The commercialization of this technology and realization of its full potential, however, depend to a great extent on the development of regenerable sorbents capable of reducing the H₂S content of gasifier fuel gas from several thousand ppmv levels down to a few ppmv at elevated temperatures (i.e., >350°C), over hundreds or even thousands of sulfidation/regeneration cycles.

Over the last two decades, development of high temperature regenerable sorbents has been pursued, primarily using various combinations of transition metal oxides. The primary focus has been directed toward application above 550°C, limiting the choice of metal oxides to those that possess favorable thermodynamic equilibria. These efforts led to the emergence of zinc-based sorbents, such as zinc titanates, as the leading candidates. However, because of problems with sorbent deterioration, further improvement is needed to minimize the overall cost of desulfurization in the IGCC process.

Recent studies on total IGCC system integration have indicated that system components become prohibitively expensive with increasing operating temperature and that the overall process efficiency gains of conducting desulfurization at above 550°C may not be sufficient to justify operation at such high temperatures. The optimum desulfurization temperature appears to be in the range of 350 to 550 °C, where technical viability and process efficiency result in lower overall process costs. In addition, because of the more favorable thermodynamic equilibria in the lower temperature range, a large number of metal oxides can be considered for coal gas desulfurization, increasing the likelihood of developing suitable sorbents.

This paper discusses the results obtained in an ongoing study geared towards developing advanced mixed-metal oxide sorbents for desulfurization of coal-derived fuel gases in the temperature range of 350 to 550 °C. The paper focuses on the study related to the development of attrition-resistant sorbents suitable for fluidized-bed application and addresses the physical and chemical characteristics of a number

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of novel sorbents as well as their sulfidation performance and regenerability. Results of sulfidation reactivity and regenerability evaluation tests with the selected sorbent formulations in a thermogravimetric analyzer (TGA), a packed-bed reactor, and IGT's High-Pressure High-Temperature (HPTR) fluidized-bed bench-scale unit, as well as the results of the ASTM D5757-95 attrition test methods performed with selected sorbents are presented and their implications are discussed.

Introduction

The need to increase the efficiency of power generation and to reduce CO₂ emissions has prompted numerous R&D efforts to make the use of coal environmentally more acceptable and economically more attractive. The last few decades have been marked by a growing interest in developing alternative technologies to conventional coal combustion. Integrated Gasification Combined-Cycle (IGCC) processes are among the leading contenders for generation of electricity from coal in the 21st century.

Coal gas desulfurization to sufficiently low levels at elevated temperatures is now recognized as crucial to efficient and economic coal utilization in IGCC systems. The implementation of hot coal gas desulfurization heavily relies on the development of regenerable sorbent materials that have high sulfur capacity and can efficiently remove H₂S (from several thousand ppmv levels down to a few ppmv) over many cycles of sulfidation/regeneration. Structural stability and good mechanical strength are also desirable features in a sorbent. Not surprisingly, only a few metal oxides can meet these stringent requirements.

The two most advanced reactor configurations for hot gas desulfurization that are currently being demonstrated in the DOE-sponsored Clean Coal Technology program include moving-bed and fluidized-bed systems. The fluidized-bed approach offers advantages over the moving-bed because of its ability to control the reactor temperature particularly during the highly exothermic regeneration step.

Research and development efforts for high-temperature desulfurization of fuel gases have been sponsored primarily by the Federal Energy Technology Center (FETC) of the United States Department of Energy (U.S. DOE). Over the last three decades a number of studies have been reported on high-temperature H₂S removal, primarily using various transition metal oxides as regenerable sorbents.⁽¹⁻⁵⁾ It must be noted, however, that much of the sorbent development work was devoted to sorbents suitable for temperatures greater than 550°C, since a higher temperature application would offer better overall process efficiency. The stringent requirement for sulfur removal efficiency at higher temperatures limited the choice of sorbents to a few metal oxides (based on thermodynamic equilibrium). The focus of much of the current research on hot coal-derived fuel gas desulfurization processes has been on the use of zinc-based sorbents, mainly because the thermodynamic equilibrium for sulfidation of ZnO is quite favorable, yielding desulfurization down to a few ppmv H₂S. However, because of zinc vaporization at elevated temperatures, zinc-based sorbents suffer from gradual loss of reactivity in the cyclic desulfurization process. Despite these shortcomings, zinc-based sorbents such as zinc ferrite (a compound of zinc oxide and iron oxide) and zinc titanate (a compound of zinc oxide and titanium oxide) have reached pilot scale testing.^(6,7) Currently, zinc titanate is considered as the prime candidate for testing in the Clean Coal Technology Demonstration Programs being sponsored by the U.S. DOE.

The overall efficiency of the IGCC process increases with increasing temperature; however, because of process equipment limitations, economic considerations, and other process variables such as fuel gas alkali content, the benefit to be gained by lower temperature application may outweigh the slight loss of efficiency, resulting in lower overall cost of electricity, leading to a conclusion that the optimum desulfurization temperature should be in the range of 350° to 550°C.⁽⁸⁾ The thermodynamic equilibria of many metal oxides improve as temperature decreases, making many metal oxide sorbents suitable for hot gas cleanup applications under these conditions. At these lower temperatures, although the extent of desulfurization may improve because of more favorable thermodynamic equilibria, the reactivity of the sorbent is greatly reduced because the kinetic mechanisms for sulfidation experience an Arrhenius type decrease with decreasing temperature. Therefore, a highly reactive sorbent is needed for these lower temperature applications.

The key characteristic of concern in the fluidized-bed application is maintenance of the physical integrity of the sorbent during the chemical transformations associated with sulfidation and regeneration. Testing appears to verify that excessive sorbent attrition results primarily from the changes in composition during chemical transformation and not from mechanical forces.^(5,9) The extreme temperature and severe chemical conditions of air/steam regeneration are deleterious to many inorganic support materials and sorbent compounds. A sorbent suitable for fluidized-bed application must, therefore, have both good thermodynamic equilibrium and initial chemical reactivity in the range of 350°-550°C, as well as acceptable long-term physical and chemical durability with a reasonable cost of production.

Program Objectives

The overall objective of this program is to develop regenerable sorbents for use in the temperature range of 350° to 550°C to remove hydrogen sulfide (H₂S) from coal-derived fuel gases using fluidized-bed reactors. The goal is to develop sorbents that are capable of removing H₂S to less than 20 ppmv over the temperature range of 350° to 550°C and pressures in the range of 1 to 20 atm, and have the chemical characteristics necessary to permit cyclic use without a drastic loss of reactivity and also the physical characteristics that are compatible with a fluidized-bed environment.

Project Description and Results

A systematic approach was used to prepare a large number of sorbent formulations for evaluation in fixed-bed and thermogravimetric analyzer (TGA) reactors, to identify the most promising sorbent formulation for high pressure fluidized-bed application in the temperature range of 350° to 550°C. Desirable characteristics of hot gas cleanup sorbents included

- Favorable sulfidation equilibrium
- High sorbent capacity
- Good reactivity toward H₂S

- Ease of regenerability
- Good attrition resistance

Thermodynamic Calculations

The initial principal criteria used for sorbent formulation was based on thermodynamic equilibrium to limit the choice of the active sorbent metals to those that can meet the stringent requirement of removing H₂S to below 20 ppmv. The thermodynamic H₂S equilibrium concentrations in a simulated fuel gas for a number of potential metal oxides were calculated at elevated temperatures (i.e., 350°-550°C) and pressure (20 bar). The metal oxides considered for this analysis included copper, zinc, iron, nickel, tin, cobalt, molybdenum, manganese, and tungsten.

The results of this analysis indicated that because of the lower temperature range (e.g., 350°-550°C), a large number of metal oxides are capable of reducing the H₂S level of the fuel gases to below 20 ppmv for IGCC application. Of course, thermodynamic predictions do not take into account the rate of approach to equilibrium (i.e., kinetic rates) and hence experimental data are still needed to confirm the extent of formation of the predicted species. Nevertheless, thermodynamics allows the investigator to determine if formation of certain compounds is favored.

Based on thermodynamic equilibria and phase stability calculations as well as available experimental data, four metals (Zn, Fe, Mn, Cu) were selected as primary desulfurization species, six other metals (Mo, Ni, Mn, Fe, Cu, Cr) as secondary species (i.e., additives) for desulfurization, and four metal species (Ti, Zr, Al, Si) were selected as supports and structure stabilizers.

Sorbent Preparation

A total of 167 sorbent formulations were prepared in this program. Each of these sorbent formulations consisted of at least one metal oxide as the reactive component (toward H₂S), at least one support material, minor additives, and binders. Each sorbent formulation represents a unique set of preparation conditions that includes sorbent composition and the subsequent thermal treatment procedures. The general breakdown of the sorbent formulations prepared, with respect to the main reactive metal oxide, is given in Table 1.

Formulation parameters considered in preparing the sorbents included nature of the reactive metal oxide component, overall sorbent composition, preparation technique, and thermal treatment (i.e., induration) conditions. For each support material several different molar ratios of metal to support was examined to determine the composition that offered the best compromise between chemical reactivity and physical strength. The amounts of additional additives (i.e., binders, porosity enhancers, etc.) were also varied to achieve the desired sorbent composition. The effect of sorbent induration (thermal treatment) condition on the crush strength or attrition resistance of the sorbent was also determined by employing different temperatures in a practical range for the specified formulation.

Table 1. Breakdown of Sorbent Formulations by Main Reactive Component

<u>Reactive Metal Oxide</u>	<u>No. of Formulations Prepared</u>
CuO	40
Fe ₂ O ₃	22
Mn ₂ O ₃	10
ZnO	95

Initially in this program, efforts concentrated on preparing sorbents with higher levels of reactive metal oxide dispersion that have higher and more stable reactivity as well as higher mechanical strength and durability. This was accomplished by the use of refractory supports/dispersants that are themselves highly resistant to sintering and deterioration. These low theoretical capacity/highly dispersed metal oxide sorbent formulations were considered to have a higher probability for maintaining stability at elevated temperatures over a large number of sulfidation-regeneration cycles. Following the preparation of low capacity sorbents, efforts were directed toward increasing the metal loading (concentration) of the sorbents to obtain higher theoretical sulfur capacity, while maintaining high mechanical strength.

Sorbent Screening

The initial selection of suitable sorbent formulations for testing was based on attrition resistance. A single-hole attrition test unit was used to measure the relative resistance of sorbents to attrition. Only those sorbents having sufficient strength were evaluated. The sorbent formulations having comparable strength to that of UCI-4169 zinc titanate sorbent were subjected to testing in the fixed-bed reactor and/or thermogravimetric analyzer (TGA) to evaluate their reactivities and sulfur sorption capacities. This commercial zinc titanate sorbent which had been extensively tested in IGT's bench-scale high-pressure/high-temperature reactor as well as Enviropower pilot-scale desulfurization units, was used as a basis to evaluate granular sorbent performance in attrition tests.

Preliminary sorbent testing included determination of the sulfidation reactivity and effective capacity of the sorbents prepared above to identify potential candidate sorbents for high pressure fluidized-bed application. Sorbent sulfidation-regeneration testing was carried out in a quartz fixed-bed reactor system at approximately one atmosphere pressure and temperatures of 350°-550°C using a simulated coal derived-fuel gas mixture (see Table 2) at a space velocity of 2000 hr⁻¹. The average particle size of the sorbents tested is in the range of 180 to 425 microns. Sulfided sorbents were regenerated using nitrogen-air mixtures at temperatures of 650°-750°C (800°C for Mn-based sorbents). The extent of desulfurization was determined by analyzing the reactor exit gas for H₂S and SO₂ with a dedicated gas chromatograph.

Table 2. Simulated Fuel Gas Composition

<u>Component</u>	<u>Composition, mol%</u>
H ₂ S	0.15-2

H ₂	10
CO	20
CO ₂	10
H ₂ O	10
N ₂	48-49.85

Initially, a number of attrition resistant low capacity sorbents were prepared and evaluated, which exhibited high reactivity toward H₂S along with acceptable durability in multi-cycle testing. Following the favorable results of the low capacity sorbents, attempts were made to improve the sulfur capacity of the sorbents, using the same sorbent preparation technique. However, most of the sorbent formulations prepared with this approach lacked sufficient strength and/or reactivity toward hydrogen sulfide.

As indicated earlier, a higher level of dispersion generally results in lower capacity and higher reactivity, while higher concentrations of the active compounds generally lead to higher theoretical sorbent capacity and lower reactivity. The key factors in the development of suitable sorbents are the stability of the sorbents through the cyclic process and the effective sulfur capacity of the sorbent (i.e., theoretical capacity x sorbent conversion at breakthrough). In order to achieve sorbent stability at the highest possible effective sorbent capacity, secondary efforts were devoted to the preparation of sorbents having higher sulfur capacity and mechanical strength. This was accomplished by extending the application of a pelletization technique previously developed for the formulation of spherical pellets (dia.=3-5 mm)⁽¹⁰⁾ to the preparation of highly attrition resistant granular (dia. = 100 to 425 µm) sorbents. This sorbent manufacturing technique has been applied to prepare over 100 formulations of copper-, iron-, manganese-, and zinc-based sorbents suitable for fluidized-bed applications at lower temperatures, i.e., T ≤ 550°C. A number of these formulations had attrition resistance similar or superior to that of the UCI-4169 zinc titanate sorbent. All sorbents that meet minimum mechanical strength requirement were evaluated for H₂S removal efficiency and effective sulfur capacity.

Rigorous testing was undertaken to determine the sulfidation reactivity and effective sulfur capacity of prepared sorbents to identify potential candidates for further evaluation in the bench-scale high pressure fluidized-bed reactor unit.

During this study, it was determined that, because of the high attrition resistance of the sorbents prepared, most of these sorbents (specially zinc-based sorbents) required an “activation step” to improve their reactivities at lower temperatures. A series of tests was conducted in the thermogravimetric analyzer reactor (TGA) to determine the optimum activation method. The results indicate that the sorbent activation technique significantly affect the reactivity of the sorbent toward H₂S. The relevant physical properties of the sorbent formulations exhibiting acceptable sulfur capacity in the packed bed tests are given in Table 3. The UCI-4169 sorbent was included for the purpose of comparison. With the exception of IGTSS-057 and IGTSS-179, all other selected sorbents were Zn-based formulations. The Mn-based IGTSS-057 and the Cu-based IGTSS-179 have the highest surface area and exhibited very high reactivities toward H₂S and did not require an activation step, as will be discussed later.

The results of three cycles of packed bed testing with the baseline UCI-4169 sorbent at 450°C are presented in Figure 1, indicating that this sorbent could achieve a sulfur loading in the range of 5-6 % at 450°C. The sulfur loading of IGTSS-122 at 450°C, after activation, is presented in Figure 2, reaching a level of 6%. However, the sulfur loading of the sorbent prior to activation was less than 1%. The IGTSS-135, IGTSS-139, and IGTSS-189 achieved sulfur loadings of less than 4%, after activation, indicating lower reactivities compared to the UCI-4169 sorbent.

The sulfur loadings for the IGTSS-314B in four (4) successive cycles, without activation, are shown in Figure 3, indicating that the reactivity of this sorbent gradually improved in the cyclic process. The sulfur loading of this sorbent during the first cycle is more than twice that of IGTSS-122 suggesting that this sorbent is more reactive than IGTSS-122 sorbent. Although the 6% sulfur loading of IGTSS-314B is similar to the UCI-4169, the very low level of H₂S pre-breakthrough and the sharp breakthrough curve are indicative of higher reactivity of the IGTSS-314B sorbent. The results obtained with the IGTSS-325A sorbent in four successive cycles are presented in Figure 4, indicating that a much higher sulfur loading of 10-12% was achieved with this sorbent, which is twice the sorbent loading achieved with the baseline UCI-4169 sorbent.

Table 3. Physical Characteristics of Selected Sorbents

Sorbent Designation	Main Reactive Metal	Hg Bulk Density ρ_b , (g/cm ³)	Apparent (Skeletal) Density, ρ_a (g/cm ³)	Porosity (%) [*]	Total Pore Surface Area (m ² /g)
IGTSS-057	Mn	1.6170	4.6936	65.55	9.2085
IGTSS-122	Zn	2.3783	4.5425	47.64	3.9135
IGTSS-135	Zn	1.4825	2.6864	44.81	0.3457
IGTSS-139	Zn	1.7841	4.6872	61.94	1.6040
IGTSS-179	Cu	3.0573	4.1724	26.73	5.2273
IGTSS-189	Zn	2.5930	4.9111	47.20	2.0690
IGTSS-314B	Zn	2.2658	4.4787	49.42	3.3383
IGTSS-325A	Zn	1.9319	4.5468	57.51	2.5935
UCI-4169	Zn	1.3795	3.1409	56.08	0.7205

Calculated as $(1 - \rho_b/\rho_a)*100$, or equivalently as $\rho_b*(\text{Total Intrusion Volume})*100$

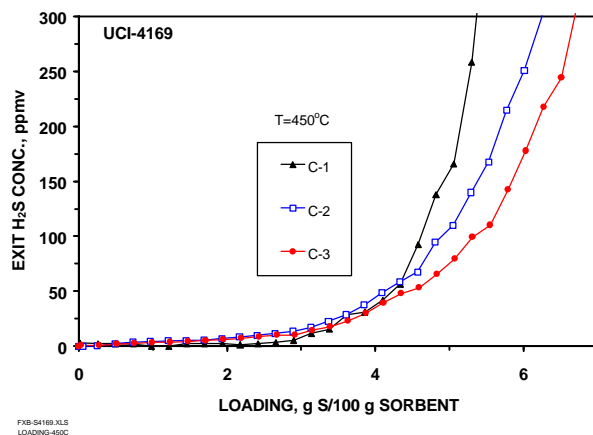


Figure 1. H₂S BREAKTHROUGH CURVES FOR THE BASELINE UCI-4169 SORBENT

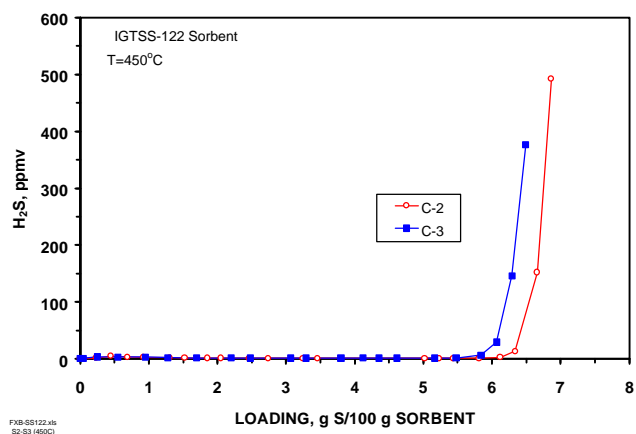


Figure 2. H₂S BREAKTHROUGH CURVES FOR THE IGTSS-122 SORBENT

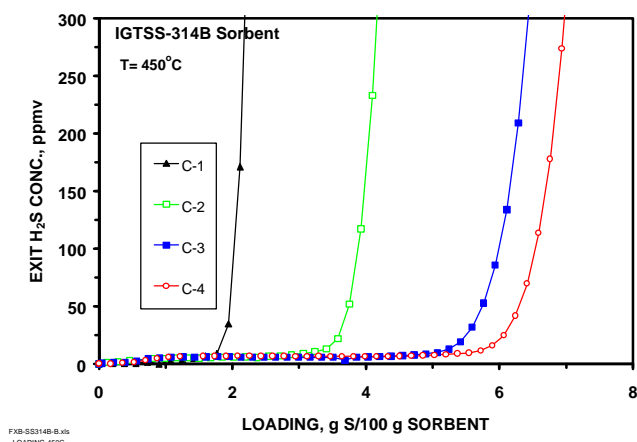


Figure 3. H₂S BREAKTHROUGH CURVES FOR THE IGTSS-314B SORBENT

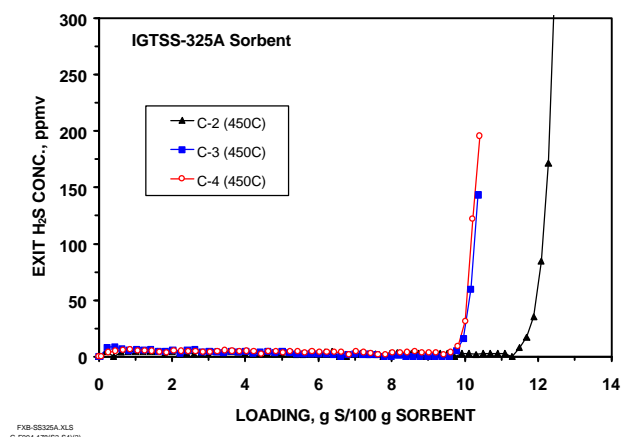


Figure 4. H₂S BREAKTHROUGH CURVES FOR THE IGTSS-325A SORBENT

A manganese-based, high sulfur capacity sorbent, IGTSS-057, achieved a total pre-breakthrough time of about six (6) hours in the second sulfidation cycle at 450°C. This time corresponds to a total sorbent conversion of nearly 47%, at a H₂S breakthrough level of 20 ppmv, and to an effective sulfur capacity of approximately 20 g S/100 g sorbent. To reduce the cycle time during testing of IGTSS-057 sorbent, the sulfidation gas space velocity was increased to 6000 hr⁻¹. The results from several cycles are reported in Figure 5. As indicated in this figure, IGTSS-057 performed consistently well even at this higher sulfidation gas space velocity, achieving effective sulfur capacities ranging from 10 to 12 g S/100 g sorbent. The regeneration tests were carried out at 800°C.

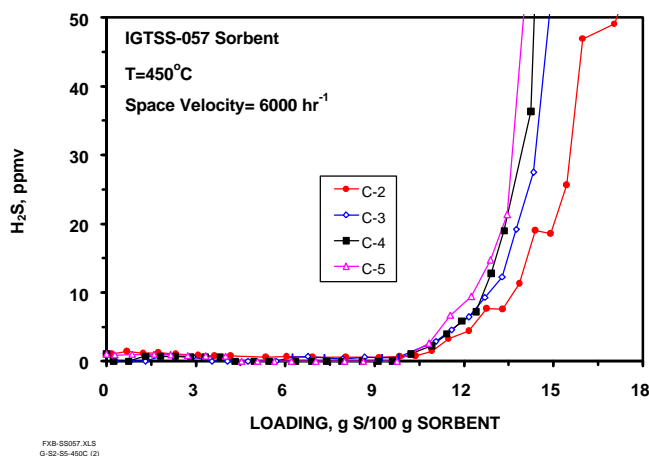


Figure 5. H₂S BREAKTHROUGH CURVES FOR THE IGTSS-057 SORBENT

The IGTSS-179, one of a number of copper-based sorbents recently developed at IGT in an on-going research program sponsored by the Illinois Clean Coal Institute (ICCI), appears to hold significant

promise for fuel gas desulfurization in the temperatures range of 350° to 550°C. As shown in Figure 6, limited multi-cycle testing in the fixed-bed reactor at 450°C indicated that this sorbent has excellent H₂S removal efficiency and an effective sulfur capacity approximating 7 grams of sulfur per 100 grams of sorbent. This effective sulfur capacity corresponds to a sorbent conversion of 70% at breakthrough. Therefore, given the high mechanical strength of this sorbent, this significant conversion is indicative of its high reactivity at 450°C. It must also be pointed out that despite its significantly high crush strength, IGTSS-179 copper-based sorbent did not require an activation step to enhance its reactivity at the lower temperature. Furthermore, the sulfidation performance of IGTSS-179 sorbent at 350°C is essentially comparable to that at 450°C.

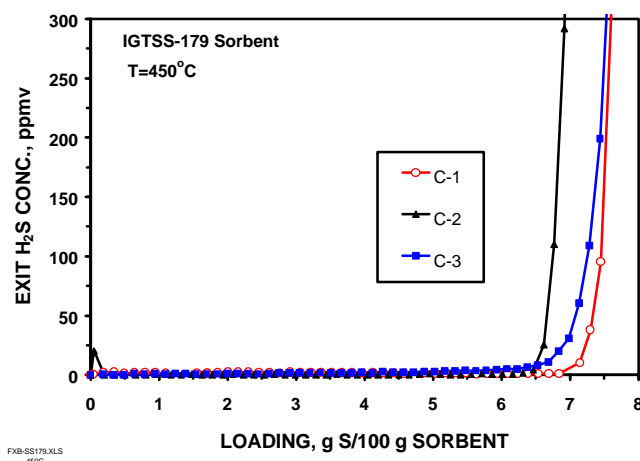


Figure 6. H₂S BREAKTHROUGH CURVES FOR THE IGTSS-179 SORBENT

Based on the results of the packed bed tests, the IGTSS-057, IGTSS-179, IGTSS-314B, and IGTSS-325A were selected for further evaluation. The attrition resistance of the selected sorbents were determined by the ASTM D5757-95 method.

ASTM Attrition Tests

The standard ASTM D5757–95 is a test method for the determination of the relative attrition characteristics of powdered catalysts by air jets. This test method is capable of providing reliable information concerning the ability of a powdered material to resist particle size reduction during use in a fluidized environment. Strictly speaking, this method is applicable to spherically or irregularly shaped particles ranging in size between 10 and 180 µm and having skeletal densities between 2.4 and 3.0 g/cm³. Nevertheless, the information it provides can be particularly valuable for research and development efforts in the area of sorbent development for fluidized-bed as well as transport reactor applications where sorbent durability during mutli-cycling is essential.

During this test a representative sample of dry powder (approximately 50 grams) is subjected to attrition by means of three high velocity jets of air. The fines generated are continuously removed from the attrition zone by elutriation into a fines collection assembly. The percent attrition loss after five (5) hours

is known as the Air Jet Index (AJI) and is calculated from the elutriated fines to give a relative estimate of the attrition resistance of the powdered catalyst as may be observed in commercial use.

The apparatus for the air jet attrition system consists of an attriting tube, a settling chamber, a fines collection assembly, and a circular orifice plate containing 3 holes and attached to the bottom of the vertical attriting tube within an air delivery manifold. The overall arrangement of the attrition unit and dimensions, as arranged at IGT, are as indicated on the schematic diagram shown in Figure 7.

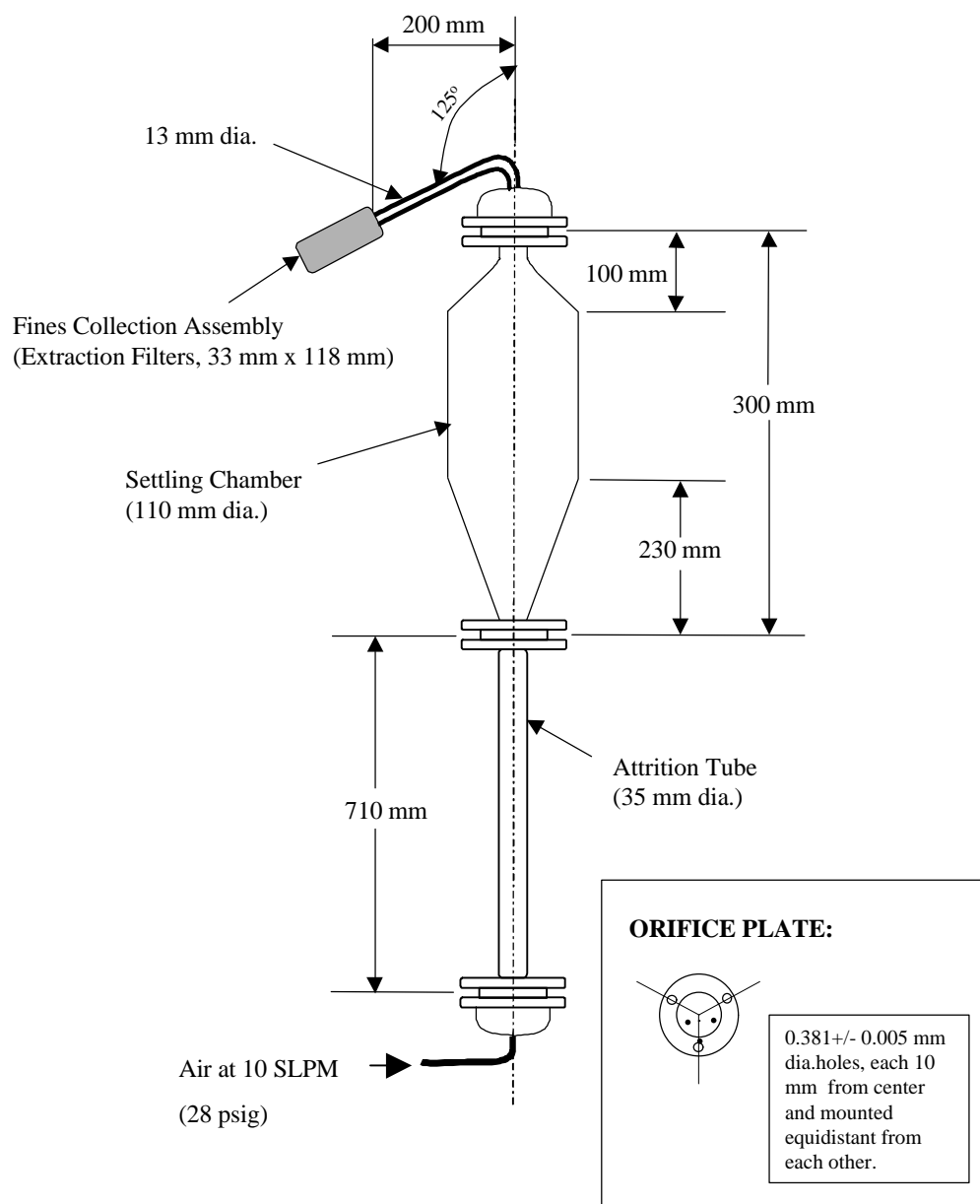


Figure 7. AIR JET ATTRITION APPARATUS

During a typical test, the system is first reassembled without the fines collection assembly. Air supply is turned on and the flow adjusted to 10.00 L/min at standard temperature and pressure (273.15 K and 101.325 kPa), resulting in a back pressure in the range of 179 to 203 kPa. This is an indication that the air jet nozzles are clean and that there are no leaks in the apparatus connections.

Two fines collection assemblies are then prepared and weighed. With the air flowing at 10 L/min and the fines collection assembly off, 50 g of the material to be tested is charged through the top of the settling chamber. The first fines collection assembly is then quickly secured to the apparatus and the timekeeping started. After exactly 1 hour from the start, the first fines collection assembly is replaced with the second one. After exactly 5 hours from the start, the second fines collection assembly is removed, the attrition unit disassembled, and the sample from the attriting tube and settling chamber recovered and weighed.

The results of an inter-laboratory study conducted by Akzo Nobel Research Facility (Pasadena, Texas), on the measurement of AJI of a fresh FCC catalyst in 3 separate tests conducted at 4 different laboratories are presented in Figure 8, to demonstrate the expected variation in the values of AJI of a selected material. These results indicate an average five-hour loss due to attrition of 20.36% with a standard deviation of 3.6%.

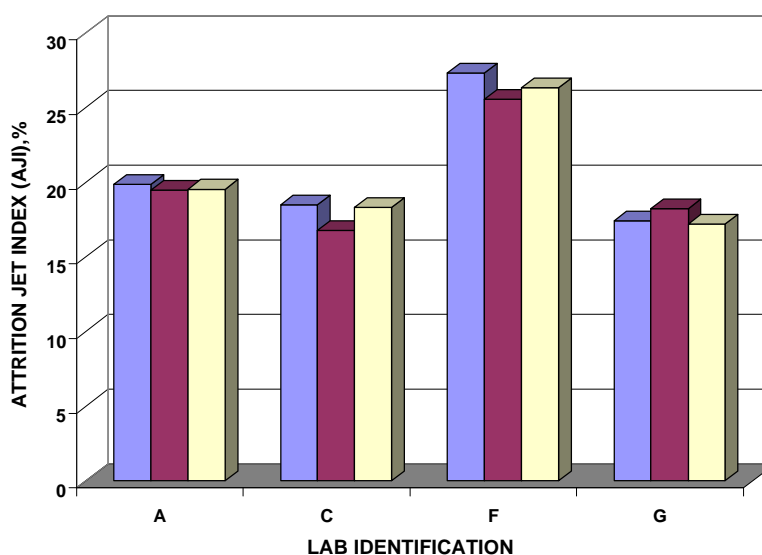


Figure 8. COMPARISON OF AJI RESULTS OF FCC CATALYST AT DIFFERENT LABORATORIES

To verify the performance of IGT's attrition unit four different materials were evaluated for attrition resistance by both IGT and Akzo Nobel Research Facility. These materials included FCC catalyst, dolomite 245, limestone 246, and UCI-4169. The results obtained with these four materials at IGT and Akzo, are presented in Figure 9, indicating that the results obtained using the IGT attrition unit are well within the experimental error of the test method.

Following the verification of IGT's test unit and experimental procedure, the attrition characteristics of the selected sorbents were determined. The results of the ASTM attrition tests are shown in Figure 10, indicating that the expected attrition loss of the zinc-based sorbents is about four times higher than the FCC catalyst. The attrition losses of the IGTSS-057 and IGTSS-179 were 39% and 10%, respectively, corresponding to about 1/2 and 1/7 of the commercial zinc titanate sorbent evaluated.

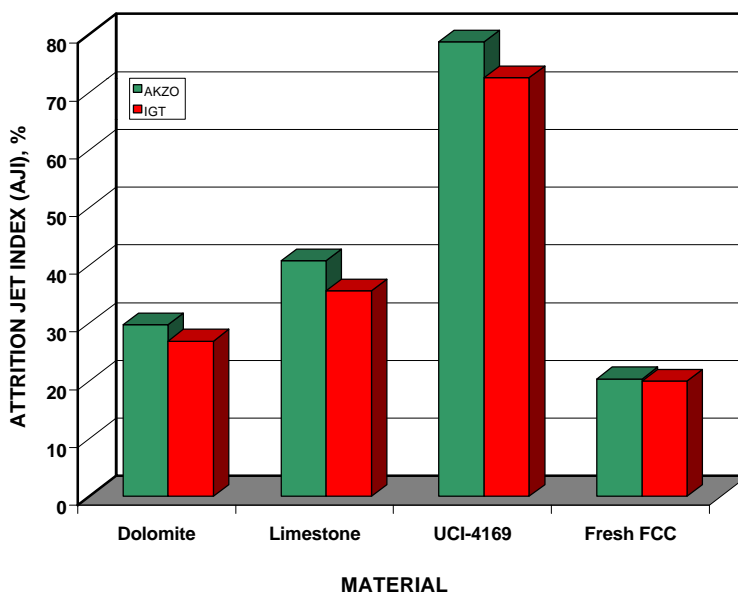


Figure 9. COMPARISON OF AJI RESULTS OF DIFFERENT MATERIALS AT IGT AND AKZO

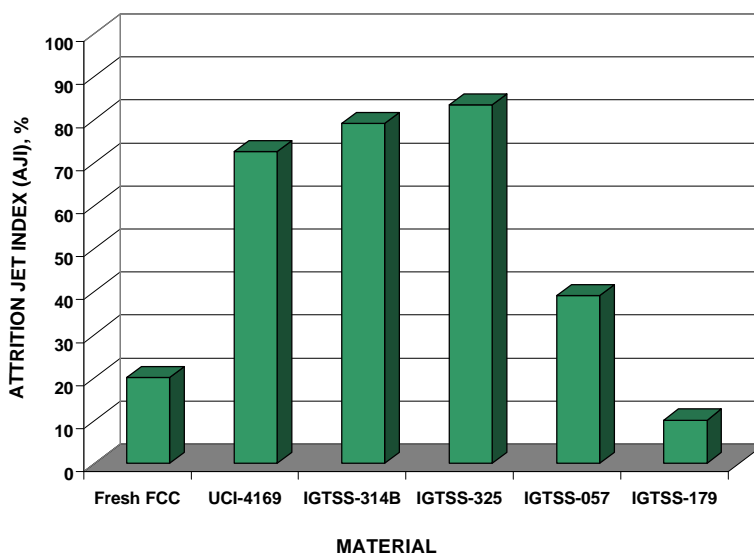


FIGURE 10. COMPARISON OF AJI RESULTS OF DIFFERENT SORBENTS

Based on the results obtained in this program, two zinc-based sorbents (IGTSS-314B, IGTSS-325A), one manganese-based sorbent (IGTSS-057), and one copper-based sorbent (IGTSS-179) were selected for the high pressure bench-scale fluidized-bed tests described below.

High Pressure Bench Scale Tests

An existing state-of-the-art bench-scale high-pressure/high-temperature batch fluidized-bed/fixed-bed reactor (HPTR) was used to carry out bench-scale testing. The test unit includes simulated hot coal-derived gas feed systems, an absorption/regeneration reactor, and associated process instrumentation and control devices. A schematic diagram of the unit is shown in Figure 11.

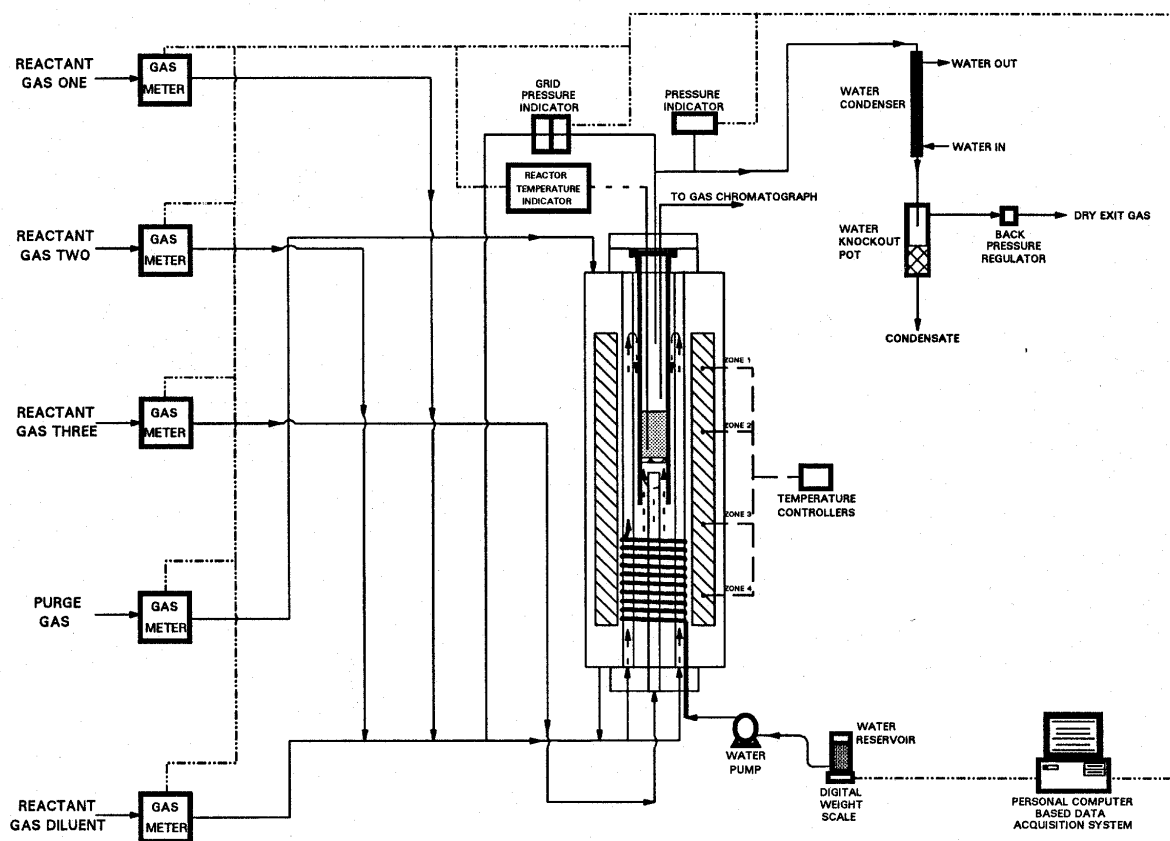


Figure 11. SCHEMATIC DIAGRAM OF THE HIGH-PRESSURE/HIGH-TEMPERATURE REACTOR (HPTR) UNIT

This is a flexible reactor system that is capable of operating either in a fluidized-bed reactor mode or in a fixed-bed reactor mode. This unit can be operated as a 2-inch or 3-inch batch fluidized-bed/fixed-bed

reactor at conditions that are expected in the hot gas desulfurization process. All the H₂S wetted parts of the reactor are constructed of quartz or ceramic material to prevent corrosion and loss of sulfur. The exit gas is sampled in the disengaging zone of the quartz reactor insert using a ceramic probe. The sampling gas stream is cooled immediately after leaving the reactor. The gas is sent directly to a dual-column gas chromatograph for analysis. The composition of the reactor exit gas is measured with a dual column gas chromatograph that is currently equipped with a flame photometric detector (FPD), a thermal conductivity detector (TCD) and auto-samplers. The FPD is used to detect low levels (0-100 ppm) of H₂S and COS while the TCD can be used to detect the sulfur dioxide (SO₂) in the exit gas.

As indicated earlier, based on the results obtained in Task 2, two zinc-based sorbents (IGTSS-314B and IGTSS-325A), one manganese-based sorbent (IGTSS-057), and one copper-based sorbent (IGTSS-179) were selected for the bench-scale fluidized-bed tests in this task. The operating conditions for evaluation of the selected sorbents are given in Table 4. The simulated coal gas composition used in these tests was similar to that reported in Table 2. The H₂S content of the feed gas in all the tests conducted in this task was 1500 ppmv. The sulfided sorbents were regenerated with a N₂/O₂ mixture containing 2-3% oxygen.

Table 4. OPERATING CONDITIONS FOR EVALUATION OF THE SORBENTS

<u>Parameter</u>	<u>Condition</u>
Sorbent Formulations	4
Mode of Operation	Bubbling fluidized bed
Sulfidation Temperature	450°C
Regeneration Temperature	650°C (850°C for IGTSS-057)
Pressure	10 atm
Particle Size	180-425 microns
Bed Height	5 cm
L/D ratio	1
Superficial Gas Velocity	20 cm/s

It should be noted that the operating condition used in this task correspond to a very shallow bubbling fluidized bed with a very short gas residence time of about 0.25 second. Therefore, the sulfur loading obtained with the sorbents in these tests is much lower than the expected loadings in commercial reactors, where the fluidized-bed height and gas residence time are significantly higher. To provide a basis for comparison of the sorbent, prior to testing of the four selected sorbents, one sulfidation test was conducted with the UCI-4169 zinc titanate sorbent at the same operating conditions.

The H₂S breakthrough curve for the UCI-4169 is presented in Figure 12, indicating a sulfur loading of about 0.5% at the test condition. The H₂S breakthrough curve for the two zinc-based sorbents developed in this program (i.e., IGTSS-314B and IGTSS-325A) are presented in Figures 13 and 14, indicating that their effective sulfur loading is generally similar to the UCI-4169 sorbent.

Significantly higher sulfur loading was achieved with the IGTSS-057 sorbent, as shown in Figure 15. Although, the manganese-based IGTSS-057 sorbent achieved a very high sulfur loading, the relatively

high H₂S pre-breakthrough concentration, and a much higher temperature of 800°C required for successful regeneration of this sorbent are undesirable characteristics of this sorbent.

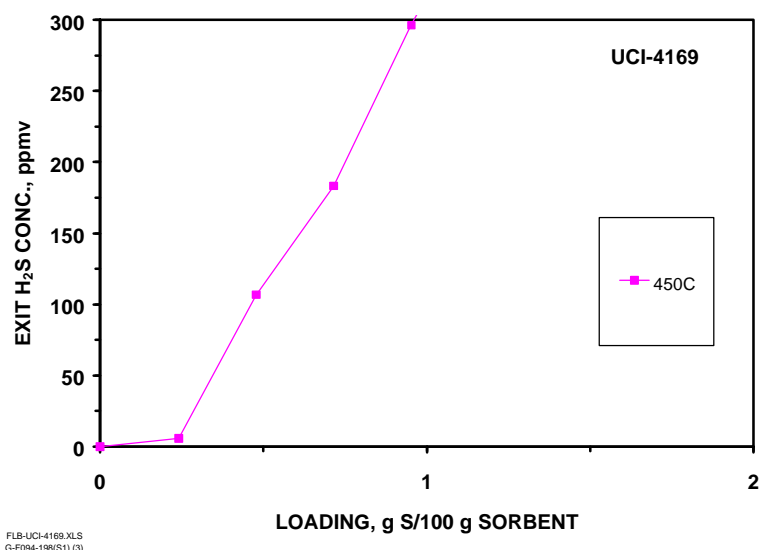


Figure 12. H₂S BREAKTHROUGH CURVES FOR THE UCI-4169 SORBENT IN HIGH PRESSURE BENCH-SCALE FLUIDIZED BED REACTOR

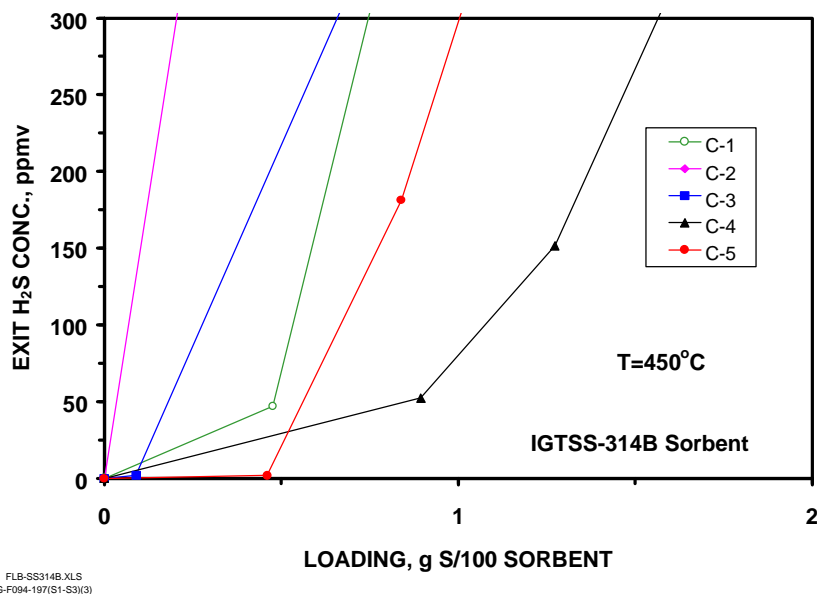


Figure 13. H₂S BREAKTHROUGH CURVES FOR THE IGTSS-314B SORBENT IN HIGH PRESSURE BENCH-SCALE FLUIDIZED BED REACTOR

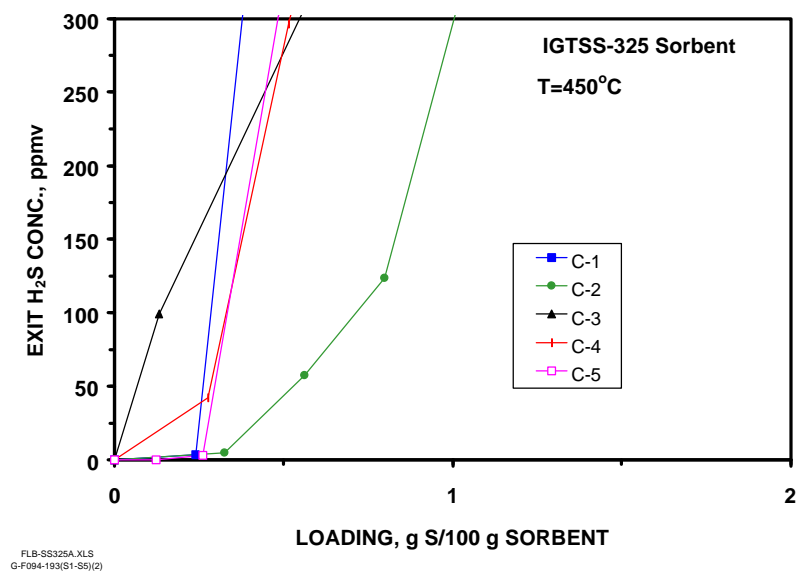


Figure 14. H₂S BREAKTHROUGH CURVES FOR THE IGTSS-325A SORBENT IN HIGH PRESSURE BENCH-SCALE FLUIDIZED BED REACTOR

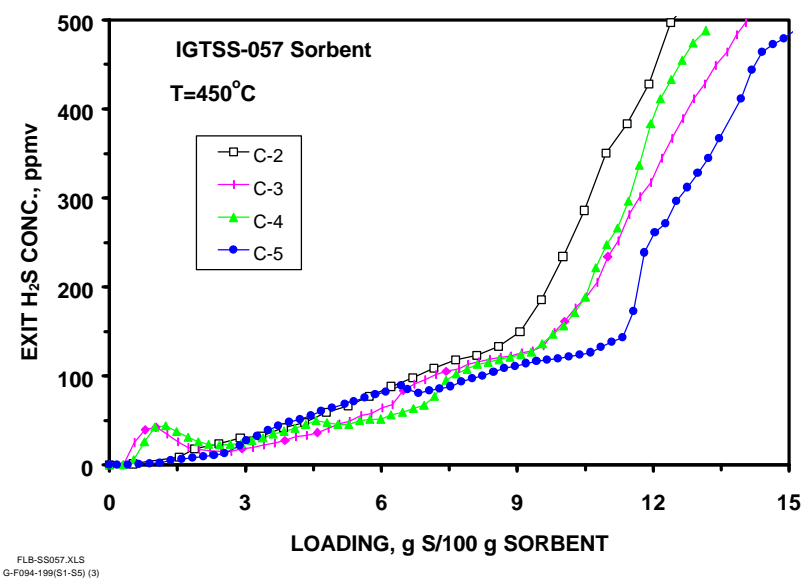


Figure 15. H₂S BREAKTHROUGH CURVES FOR THE IGTSS-057 SORBENT IN HIGH PRESSURE BENCH-SCALE FLUIDIZED BED REACTOR

A sulfur loading of 4-6% was achieved with the copper-based IGTSS-179 sorbent in cycles 2 through 5, as shown in Figure 16. To improve the fluidization behavior of the IGTSS-179 sorbent, this sorbent was

mixed with the IGTSS-135 sorbent (which has been shown to have very low reactivity toward H_2S). As shown in Figure 16, the reactivity of the IGTSS-179 sorbent appears to improve during the cyclic process, and the H_2S pre-breakthrough concentration is well below 20 ppmv. The high reactivity of the IGTSS-179 sorbent, coupled with the very high attrition resistance, indicates that IGTSS-179 is the best sorbent formulation developed in this program.

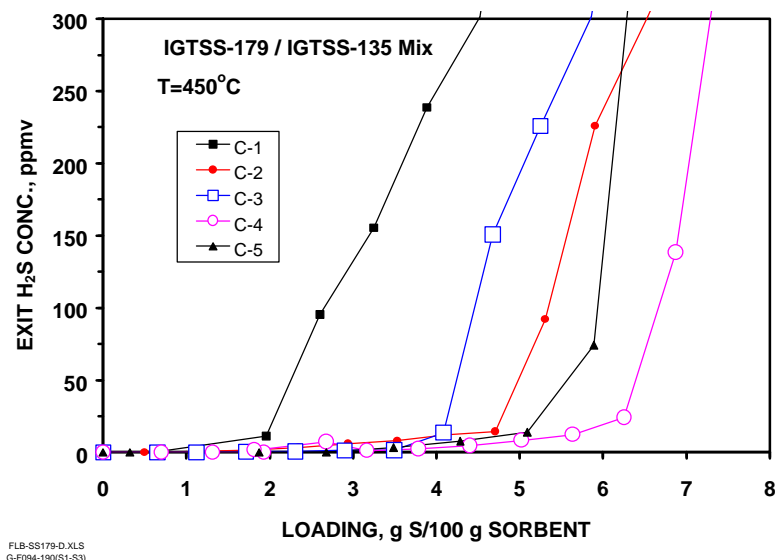


Figure 16. H_2S BREAKTHROUGH CURVES FOR THE IGTSS-179 SORBENT IN HIGH PRESSURE BENCH-SCALE FLUIDIZED BED REACTOR

Compared to the UCI-4169 baseline sorbent, the IGTSS-179 is at least seven times more reactive and seven times more attrition resistant. Therefore, further evaluation of this sorbent is recommended to determine the chemical stability and physical durability of the sorbent in a “life-cycle” test.

Future Activities

Discussion are currently underway with FETC to continue the work to demonstrate the long term durability and chemical reactivity of the “best” sorbent formulation in a “life-cycle” test to be conducted in IGT’s high pressure fluidized bed bench scale unit.

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